Micropollutants removal from secondary-treated municipal wastewater using weak polyelectrolyte multilayer based nanofiltration membranes

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ABSTRACT

Nanofiltration (NF) is seen as a very promising technology to remove micropollutants (MPs) from wastewater. Unfortunately this process tends to produce a highly saline concentrate stream, as commercial NF membranes retain both the MPs and most of the ions. The high salinity makes subsequent degradation of the MPs in a bioreactor very difficult. The main goal of this study is to prepare and study a NF membrane that combines a low salt rejection with a high MPs rejection for the treatment of secondary-treated municipal wastewater. This membrane was prepared using layer by layer (LbL) deposition of the weak polycation poly(allylamine hydrochloride) (PAH), and the weak polyanion poly(acrylic acid) (PAA), on the surface of a hollow fiber dense ultrafiltration (UF) membrane. The ionic strength of the coating solutions was varied and properties of the formed polyelectrolyte multilayers (PEMs), such as hydration, hydrophilicity, hydraulic resistance and ions retention were studied. Subsequently we tested the apparent and steady state rejection of MPs from synthetic wastewater under cross-flow conditions. The synthetic wastewater contained the MPs Diclofenac, Naproxen, Ibuprofen and 4n-Nonylphenol, all under relevant concentrations (0.5–40 μg/L, depending on the MP). PEMs prepared at lower ionic strength showed a lower hydration and consequently a better retention of MPs than PEMs prepared at higher ionic strengths. A strong relationship between the apparent rejection of MPs and their hydrophobicity was observed, likely due to adsorption of the more hydrophobic MPs to the membrane surface. Once saturated (steady state), the molecular size of the MPs showed the best correlation with their rejection, indicating rejection on the basis of size exclusion. In contrast to available commercial NF membranes with both high salt and MP rejection, we have prepared an unique membrane with a very low NaCl retention (around 17%) combined with a very promising removal of MPs, with Diclofenac, Naproxen, Ibuprofen and 4n-Nonylphenol being removed up to 77%, 56%, 44% and 70% respectively. This membrane would allow the treatment of secondary treated municipal wastewater, strongly reducing the load of MPs, without producing a highly saline concentrate stream.

1. Introduction

Over the last few years, a great concern has been highlighted regarding the occurrence of micropollutants (MPs) in aquatic resources and the subsequent effects on humans and the environment [1]. In addition to the 45 priority substances on the European Watch List (Directive, 2013) [2], an additional watch list of 10 priority substances that should be monitored within the European Union was recently included in Decision 495/2015/EU [3] indicating the growing attention to this issue. In this regard, effluents of wastewater treatment plants have been recognized as the main entry point of these compounds into the aquatic environment [4]. Conventional treatment methods do not lead to sufficient removal of MPs, and adding additional steps during wastewater treatment is seen as the most promising way to reduce the release of these compounds into surface waters [5]. To date, identification of technically and economically feasible advanced wastewater treatment options for the elimination of MPs from secondary-treated effluent is ongoing. Adsorption processes, advanced oxidation processes (AOPs) and membrane filtration are important examples of such technologies. Among these options, listed in Table 1, membrane technologies such as nanofiltration (NF) and reverse osmosis (RO) have attracted a great interest because of high removal rates (> 90%) of low molecular weight MPs, excellent quality of treated effluent, modularity and the ability to integrate with other systems. On the other hand,

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Table 1
The most-frequently used treatment technologies for removal of MPs from secondary-treated municipal wastewater.

Category of tertiary treatment	Subcategory	Advantages	Disadvantages/limitations	References
Advanced oxidation processes (AOPs)	Ozonation	Remarkable capability for removing most of the pharmaceuticals and industrial chemicals	As O_3 is a highly selective oxidant, ozonation often cannot ensure the effective removal of ozone-refractory compounds such as Ibuprofen.	[36]
		It has been successfully applied in many full-scale applications in reasonable ozone dosages.	Ozonation produces carcinogenic bromate from bromide that exists in secondary-treated effluents.	[36,37]
	Fenton oxidation	This kind of system is attractive because it uses low-cost reagents, iron is abundant and a non toxic element and hydrogen peroxide is easy to handle and environmentally safe.	In this process, the low pH value often required in order to avoid iron precipitation that takes place at higher pH values. This process is not convenient for high volumes of wastewater in full-scale applications.	[2,38]
	Heterogeneous photocatalysis with TiO_2	The principle of this methodology involves the activation of a semiconductor (typically TiO_2 due to its high stability, good performance and low cost) by artificial or sunlight.	The need of post-separation and recovery of the catalyst particles from the reaction mixture in aqueous slurry systems can be problematic. The relatively narrow light-response range of TiO_2 is one of the challenges in this process. This process is not convenient for high volumes of wastewater in full-scale applications.	[38]
	Photolysis under ultraviolet (UV) irradiation	Photo-sensitive compounds can be easily degraded with this method.	UV irradiation is a high-efficient process just for effluents containing photo-sensitive compounds. This process is not convenient for high volumes of wastewater in full-scale applications. The addition of H_2O_2 to UV is more efficient in removing MPs than UV alone, but UV/H_2O_2 is a viable solution for the transformation of organic MPs with low O_3 and $^{\cdot}OH$ reactivity.	[38]
	Ultrasound irradiation (Sonolysis)	It is a relatively new process and therefore, has unsurprisingly received less attention than other AOPs. But it seems that this process is economically more cost-effective.	There are very few studies and consequently rare experience about sonolysis of the effluent MPs.	[39]
Adsorption processes	Adsorption processes with activated carbon	It has been identified as powerful and easily adjustable technology to remove MPs.	This process should be followed by a final polishing step (sand filtration or UF membranes) to retain adsorbed contaminants and spent activated carbon. So higher energy requirements of UF membrane and the relatively high carbon dosage (up to 20 mg/L) necessary to achieve the required MPs removal.	[5]
		Large-scale trials have not only demonstrated excellent removal (> 80%) of a broad range of micropollutants, but also contributed to reducing the effluent toxicity.	In the case of “granular activated carbon”, a regeneration process of the spent carbon is required, while spent "powdered activated carbon" must be incinerated or dumped after filtration process.	
Membrane filtration	RO and NF membranes	These processes have attracted a great interest because of higher removal rate of low molecular weight PSs, excellent quality of effluent, modularity and ability to integrate with other systems despite their fouling problems.	High quantities of cations, anions, sulfate, MPs, etc. in the concentrate produced in NF and RO processes compel wastewater managers and decision makers to treat it with complicated processes specially in the case of full-scale applications. High energy consumption (about 4.7 and 3.4 kW h/m^3), high capital (334.3 and 338.2 \$/m^3/d) and operational costs (0.72 and 0.57 \$/m^3) of RO and NF membranes, respectively, and their problematic fouling issues may preclude membrane treatment as an option.	[6,40,41]

fouling is often a real problem for these membrane processes [6]. A lower energy consumption and higher permeate fluxes for NF membranes in comparison to RO membranes have encouraged the use of NF membranes for several commercial purposes, such as wastewater reclamation, water softening, and desalination [7,8]. Also for MPs removal, NF membranes are seen as a more cost effective alternative to RO membranes.

A major drawback of these pressurized membranes is the production of a waste stream (concentrate) which typically has a volume of up to 10–20% of the original wastewater volume [9]. This stream is rich in dissolved organic compounds, heavy metals and inorganic salts of Na^+, Cl^-, Ca^{2+}, Mg^{2+} and SO_4^{2}, and also contains the removed organic MPs [10]. Since the discharge of untreated concentrate poses a significant risk to the environment, increasing attention has been paid to this issue in recent years. Today, various methods exist for the disposal and management of concentrate produced from membrane plants such as discharge to surface water, wastewater treatment plants and deep wells, land application, and evaporation ponds. The removal of specific compounds from this unwanted stream may be performed by using activated sludge systems which are more cost-effective compared to other treatment options such as oxidation processes, adsorption or ion exchange [11–13]. The biological treatment of the concentrate stream strongly depends on its chemical composition which is often influenced by the membrane recovery rates (or expressed as the volume reduction factor) [11,14]. Azaïs et al. [14] investigated the chemical composition of the concentrate stream produced from NF90 membranes, treating secondary-treated wastewater, at different volume reduction factors (from 2 to 10). They reported the average composition of the NF concentrates: conductivity from 2 to 5.1 mS cm^{-1}, dissolved organic compound (DOC) from 12 to 48 mg L^{-1}, chemical oxygen demand (COD) from 49 to 180 mg L^{-1}, and MPs concentrations multiplied by a factor of 3–7 compared to those encountered in the secondary-treated wastewater. From this bibliographic review, there is still a lack of knowledge on the favorable concentration of MPs for their efficient biotic removal during the concentrate's biological treatment. Apart from that, the main limitation in biological treatment of the concentrate is its high salinity (> 1%) which is harmful to the bacteria because the increased osmotic pressure damages bacterial cell walls (plasmolysis of the organisms at high salt concentrations) [9]. More information about detrimental levels of the salinity on the performance of activated sludge reactors is given in Section S1 in Supplementary data. Therefore, in the present work, we propose to make use of NF membranes with a much lower rejection of salts than most of the commercial NF membranes, with the aim to achieve easy and feasible biological treatment of the generated concentrate stream. For this purpose, one requires NF membranes with a low ion rejection (< 30%) and a high rejection of MPs (> 80%), a membrane that is currently not commercially available.

Recently, the development of better performing NF membranes has been an important on-going challenge, especially because a higher flux normally goes hand-in-hand with lower selectivity and vice versa. To achieve membranes with a high flux combined with a high selectivity, it is required to establish a thin and defectless separation membrane on top of a highly permeable and mechanically robust support [15]. To prepare such promising membranes, some techniques have been developed for membrane surface modification such as grafting and interfacial polymerization [16,17]. Since these processes are laborious, costly and rely on environmentally unfriendly solvents [18], the method chosen for this study is a polyelectrolyte layer by layer (LbL) deposition technique. In this approach, a substrate is alternatively exposed to polyanions and polycations to build polyelectrolyte multilayers (PEMs) of a controllable thickness [15]. Nowadays, the LbL adsorption of polyelectrolytes (PEs) is performed by some developed methods like dip-coating [19], spray coating [20] and spin coating [21] to make polyelectrolyte multilayer membranes. Indeed, PEM based membranes can be considered as functionalized membranes with a strong potential for application in, for example, desalination [22], Heavy metals removal [23], alcohol/water separation [24], filtration of sludge supernatant [25] and recently in MPs removal [26,27]. In addition to the electrostatic interactions present in PEMs [28,29], other interactions such as hydrophobic interactions [30], hydrogen bonding [31] and chemical crosslinking [7] can play a role. As such, the choice of convenient PEs is the distinguished parameter that it affects all above-mentioned driving forces.

Apart from the choice of PEs, it has been demonstrated that multiple parameters such as pH, ionic strength, and charge density, can influence the LbL process and the resulting PEMs [32–34]. This versatility makes it possible to prepare PEM based membranes that are really optimized for a certain application. The application of PEMs-based membranes has been recently investigated in MPs removal by some researchers [26,27]. For the first time, Joris de Grooth et al. [26] obtained excellent retentions for both positively and negatively charged MPs in NF Membranes made by Polycation/Polyzwitterion/Polyanion Multilayers. Unfortunately, neutral and small micropollutants were hardly retained. Then, in the research of Ilyas et al. [27], a PEM based NF membrane made by LbL assembly of weak PEs was developed with interesting properties for the removal of MPs from wastewater effluents. The membrane combined a low ion rejection, with a good MP rejection (60–80%) even for small and neutral MPs, providing for the first time a membrane that could remove MPs without producing a highly saline waste stream. This membrane was only studied under ideal conditions and for unrealistically high MP concentrations (mg/mL). The performance under conditions relevant for wastewater treatment still needs to be studied.

In the present study, we aim to study the membrane developed by Ilyas et al. [27] under realistic conditions for municipal wastewater treatment, studying the ion rejection, and the rejection of relevant MPs within a complex water composition. Furthermore, we have continued to optimize the membrane performance by studying the impact of ionic strength on the properties of the formed PEMs in the case of salts and MPs retention. The polymers used here are two weak oppositely-charged PEs, with physical structures illustrated in Fig. 1, named Poly (allyl amine) hydrochloride (PAH) containing a primary amine ($–NH_3^+$) (weak cationic) and poly (acrylic acid) (PAA) with a weak anionic carboxylic acid group. The PEM based active separation layers were coated onto Hollow fiber dense UF membranes by LbL adsorption.

The removal of relevant MPs including three analgesic and anti-inflammatory pharmaceutical compounds (Diclofenac, Naproxen and Ibuprofen) and one endocrine disrupting compound (4n-Nonylphenol) from secondary-treated municipal wastewater was studied. The main objective of this study was to demonstrate the possibility to prepare LbL-made NF membranes with a high rejection of MPs and a low retention of salts from secondary-treated municipal wastewater. This strategy would lead to make membrane processes with a low-saline concentrate stream which is more convenient for the biological treatment in activated sludge systems.

2. Experimental

2.1. Chemicals

All chemicals used in this study including MPs (listed in Table 2

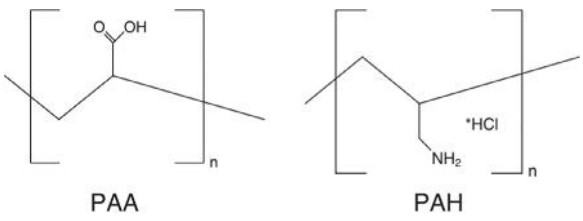

Fig. 1. Molecular structure of PAA and PAH used in this study [35].

Table 2
Physico-chemical characteristics of target MPs in this study [6,42,45,48,57–59].

Compound	CAS number	Formula	Molecular Weight (g mol^{-1})	Solubility in water at 25 °C (mg L^{-1})	Vapor pressure (mm Hg), at 25 °C	Boiling point (°C)	log K_{OW}	log D (pH:7)	pKa	Minimum Projection Area ($Å^2$)	Molar volume (cm^3/mol)	Molecular dimension Length × Width × Height (nm)	Molecular structure
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	2.4	1.59E− 7	412 ± 45	4.548	1.77	4.18	43.3	182	0.829 × 0.354 × 0.767	
Naproxen	22204-53-1	$C_{14}H_{14}O_3$	230.26	16	3.01E− 7	404 ± 20	3.18	0.34	4.3	34.8	192.2	1.37 × 0.78 × 0.75	
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.28	21	1.39E− 4	320 ± 11	3.97	0.77	4.47	35.4	200.3	1.39 × 0.73 × 0.55	
4n-Nonylphenol	104-40-5	$C_{15}H_{24}O$	220.35	6.35	8.53E− 5	331 ± 11	6.142	6.14	10.15	NA	279.8	1.179 × 0.354 × 0.519	

NA: not available in literature.

with their physical and chemical properties), two weak PEs (PAH with Mw = 15,000 g mol^{-1} and PAA with Mw = 15,000 g mol^{-1})., $NaNO_3$ as a background electrolyte, all salts ($CaCl_2$, $CaCl_2{\cdot}2H_2O$, Na_2SO_4, NaCl, K_2HPO_4, $MgSO_4{\cdot}7H_2O$), peptone, meat extract and urea) were obtained from Sigma–Aldrich. The concentration of PAH and PAA in PE solutions were always 100 mg L^{-1} with pH of 6 for both PEs and they were prepared in two ionic strengths of 5 and 50 mM $NaNO_3$. By the way, for evaluating salt rejection, concentration of all salts in feed solution of all membranes were adjusted at 5 mM ($CaCl_2$: 554.9, Na_2SO_4: 710.2, and NaCl: 292.2 mg L^{-1}). Furthermore, Milli Q water (18.2 MΩ cm) was used to prepare PE and salts solutions, rinse and measure parameters including membranes permeability and resistance.

The hydrophobicity of MPs is expressed as the log D (logarithm of the octanol-water distribution coefficient), or the log Kow (logarithm of the octanol-water partition coefficient). However, log D appears to be a better hydrophobicity indicator than log Kow and can be used to evaluate the hydrophobicity of MPs at any pH value [42]. In this regard, compounds with log D > 2.6 are referred to as hydrophobic that prefer to accumulate in solid phases instead of being soluble in the aqueous phase, and hydrophilic when log D ≤ 2.6 [43]. Hence, according to the values presented in Table 2 for log D, 4n-Nonylphenol is classified as hydrophobic, in contrast with the rest of MPs, and is therefore expected to adsorb to the surface of hydrophobic membrane surfaces by hydrophobic interactions.

Minimum projection area (MPA), calculated from the van der Waals radius, is defined as the smallest two-dimensional projection area of a three-dimensional molecule. By projecting the molecule on an arbitrary plane, two-dimensional projection area can be calculated and the process is repeated until the minimum of the projection area is obtained (Fig. 1S in Supplementary Data) [44,45].

2.2. Synthetic wastewater

Synthetic secondary-treated municipal wastewater was prepared according to the OECD protocol [46,47]. In order to make it, firstly, a mother stock solution was made in 1 L of tap water containing 160 mg peptone, 110 mg meat extract, 30 mg urea, 28 mg K_2HPO_4, 7 mg NaCl, 4 mg $CaCl_2{\cdot}2H_2O$ and 2 mg $MgSO_4{\cdot}7H_2O$ [46,47]. Then the daughter stock solution was made in an effective volume of 5 L. This synthetic wastewater contained 50 ± 2 mg L^{-1} of COD, 10 ± 1 mg L^{-1} of total nitrogen (TN) and 1 ± 0.1 mg $P\text{-}PO_4^{3-}$. L^{-1}. Moreover, daughter stock solutions of each target MP were prepared separately in Milli-Q water from their individual mother stock solutions, prepared in methanol at a concentration of 1 g L^{-1}. Regarding the review paper published by Luo et al. [48], and also on the basis of available data in literature about the concentration of target MPs in effluents of municipal wastewater treatment plants treated with conventional activated sludge systems (Fig. 2), final concentrations of Diclofenac, Naproxen, Ibuprofen and 4n-Nonylphenol in feed solution were considered 0.5, 2.5, 40 and 7 μg L^{-1}, respectively. To avoid possible bacterial biodegradation and photodegradation, mother stock solutions of MPs were stored in amber glass bottles and kept in freezer (− 18 °C) while synthetic wastewater and daughter stock solutions of MPs were prepared immediately before starting the filtration process in aluminum-wrapped glass containers.

2.3. COD, TN, and $P\text{-}PO_4^{3-}$ measurements

Samples were firstly filtered through 0.45 μm glass fiber filters (Sartorius, Göttingen, Germany). Then, the analysis process were done using HACH LANGE kits for COD, TN, and $P\text{-}PO_4^{3}$, along with DR3900 Benchtop VIS Spectrophotometer equipped with HT200S oven (HACH LANGE, Germany). These parameters were measured in duplicate and the average values were presented.

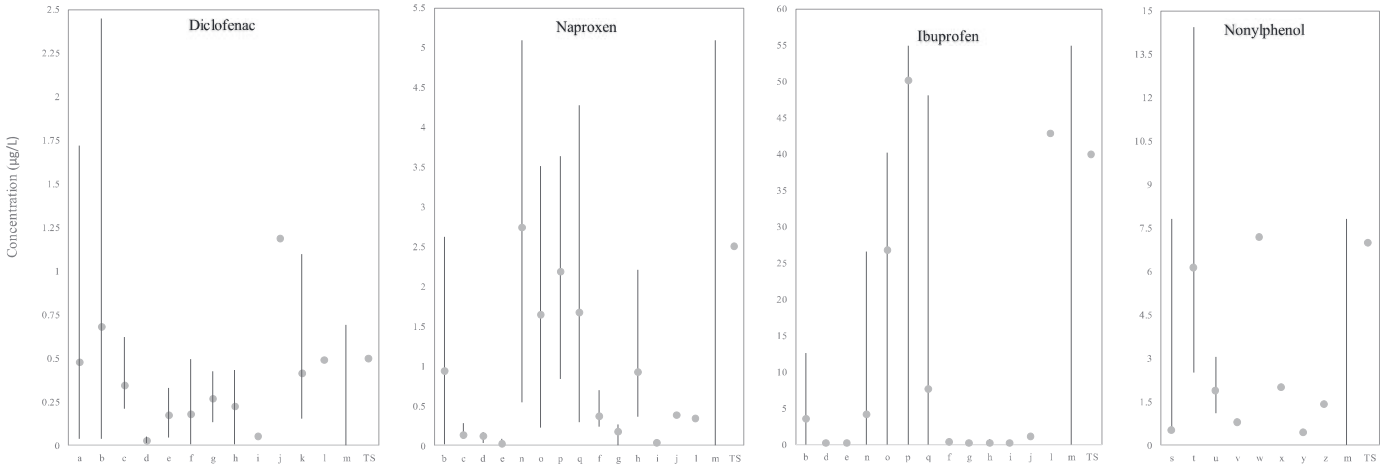

Fig. 2. Concentration range of target MPs in secondary-treated effluent of conventional wastewater treatment plants s found in literature (TS: This study, References: [a] [60], [b] [61], [c] [62], [d] [63], [e] [64], [f-g] [65], [h] [66], [i] [67], [j] [4], [k] [68], [l] [69], [m] [48], [n-o-p-q] [70], [s] [71], [t-u] [72], [v] [73], [w] [74], [x] [75], [y] [76], [z] [77]).

2.4. Membrane characteristics

Hollow fiber dense UF membranes (Hollow Fiber Silica (HFS)) with a molecular weight cutoff of 10 kDa and an inner diameter of 0.79 mm prepared from poly(ether sulfone) with a sulfonated poly(ether sulfone) separation layer (SPES) were kindly provided by Pentair X-Flow (The Netherlands). This membrane is designed for inside-out filtration. The presence of the anionic SO_3^- group on the sulfonated polymer backbone allows for a good adhesion of PEMs.

2.5. Preparation of PEMs via dip-coating

Dip-coating involves the sequential immersion of a given substrate into solutions with oppositely charged polyelectrolyte solutions, typically with one or more rinsing steps in between. By this simple procedure, transport of the polymer to the substrate surface is mainly based on diffusion. As we immerse the hollow fiber support membrane completely in the coating solution, PEs deposition is not limited to the inner surface of the membrane only and the whole porous structure can be coated by the PEs [49]. In this study, hollow fibers and silicon wafers were coated according to the protocol described by de Grooth et al. [50]. Considering the negatively charged surface of these membranes (zeta potential of − 25 mV in 5 mM KCl [51]), the first applied polyelectrolyte should have an opposite charge, here PAH. In this study, we have used silicon wafers in order to follow the growth and thickness of adsorbed PEs which are difficult parameters to be monitored in coated HFS membranes.

Before coating, wetting of 20-cm hollow fibers were done in 15 wt% ethanol in water overnight. Then wet fibers were rinsed with deionized water three times followed by three times rinsing in the background electrolyte solution ($NaNO_3$). The used silica wafers were effectively cleaned by a 10-min plasma treatment using a low-pressure Plasma Etcher (Femto model) purchased from Diener Electronics, leading to a reproducible negative charge at the surface of all wafers.

Afterwards, fibers/wafers were completely immersed in a 0.1 g L^{-1} polycation solution (PAH) with a pH of 6 and ionic strengths of 5 or 50 mM $NaNO_3$ at room temperature. After 30 min, to remove polymer chains that are loosely attached to the pre-adsorbed polymer layer, fibers/wafers were rinsed in two separate solutions containing only $NaNO_3$ with an ionic strength similar to that of the coating solution for 15 min per solution. The rearrangement of the polymer chains that occurs during the rinsing step, leads to increased stability and improved thickness control [52]. Then to form the first bilayer of PAH/PAA, fibers/wafers were dipped for 30 min in 0.1 g L^{-1} polyanion solution (PAA) with pH of 6 and two ionic strengths of 5 or 50 mM $NaNO_3$ and rinsed again in two separate background solutions exactly as before. This procedure was repeated up to the formation of 13 layers of PEs i.e. $(PAH/PAA)_6$-PAH. After each step of coating, three samples of fibers/wafers were picked up for future experiments.

To avoid pore collapse, coated fibers were kept in glycerol/water (15 wt%/85 wt%) solution for at least 4 h and dried overnight under ambient conditions. These coated fibers were subsequently potted in single fiber plastic modules of 15 cm in length, with a hole in middle and two heads potted with an epoxy resin. Before filtration, these modules were put in deionized water overnight to help opening of blocked pores.

2.6. Spectroscopic ellipsometry (hydration measurement)

Ellipsometry is a very sensitive optical technique based on detecting the changes in polarization state of a light beam upon reflection from the sample of interest [53]. In the present work, dry and wet thicknesses of deposited multilayers on the surface of plasma-treated silicon wafers were measured using an in-situ Rotating Compensator Spectroscopic Ellipsometer (M-2000X, J. A. Woollam Co, Inc.) operated in a wavelength range from 370 to 920 nm at incident angles of 65°, 70° and 75°. Thickness measurements were calculated using the Cauchy model for ellipsometric parameters (Δ and ψ) and refractive index (n) was taken from independent measurements using a standard laboratory refractometer (Carl Zeiss). Finally, data obtained on three parts of each wafer were reported as a mean dry thickness ± standard deviation [54], and subsequently hydration ratio (swelling degree) was determined using Eq. (1) by means of resulted wet thickness of multilayers [55].

$$\text{Hydration ratio} = \frac{d_{swollen} - d_{dry}}{d_{dry}} \quad (1)$$

Where, $d_{swollen}$ is the wet thickness of multilayers measured in the presence of milli-Q water in nm, and d_{dry} is dry thickness of multilayers in nm.

2.7. Contact angle

In order to measure the hydrophilicity of coated fibers/wafers, optical contact angle measurements were performed on an OCA15 plus instrument (Dataphysics Inc.) using a sessile drop method. Sessile drops of 2 µl and 0.4 µl deionized water for coated wafers and fibers, respectively were used to measure the contact angle. The small droplets were essential to be able to obtain a reliable contact angle from the hollow fibers. The hollow fiber surface is curved, but for such a small

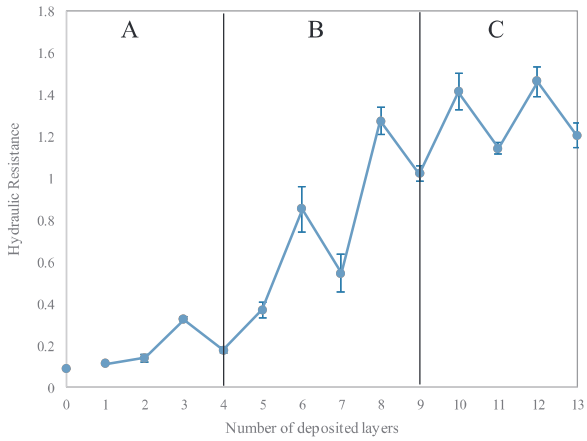

Fig. 3. Changes in hydraulic resistance of virgin and coated membrane ($\times 10^{14}\ m^{-1}$) after deposition of each additional monolayer for PAH/PAA) multilayers prepared in ionic strength of 50 mM $NaNO_3$.

droplet the effect of curvature can be neglected when determining the contact angle. These measurements were carried out four times for each sample (at 20 °C), and the average and standard deviation are reported. The measurement was carried out five seconds after the bubble was placed on the surface of the wafers/fibers. We evaluated the hydrophilicity of coated wafers before and after immersion in the feed solution (synthetic wastewater containing target MPs) for 48 h, and coated fibers before and after filtration of the feed solution (see Section 2.8). Immersed silicon wafers were dried with nitrogen gas, and the fouled fibers were dried for 24 h at room temperature (20 °C) before the measurements.

2.8. Membrane performance

2.8.1. Water permeability & hydraulic resistance

To evaluate the water permeability and thereby the resistance of coated membranes, a lab-scale filtration system with dead-end mode was used. The pure water flux was measured at 20 °C with demineralized water at a trans-membrane pressure (TMP) of 1.5 bar (Eq. (2)). Then from the water flux, the membrane resistance was obtained using Eq. (3).

$$J = \frac{Q}{A_{mem}} \tag{2}$$

$$R = \frac{\Delta P}{\mu \times J} \tag{3}$$

Here, J is water flux in m^3/m^2 s, Q is volume flow in m^3/s, A_{mem} is membrane area in m^2, μ is the dynamic viscosity of the feed in Pa s, and ΔP is the TMP in Pa. From each deposited layer of polymer, at least two modules were tested and the average of the permeability and resistance with standard deviation are reported.

2.8.2. Salts and MPs retention

For salts and MPs retention measurements, another lab-scale filtration set-up was used in a cross-flow mode at a TMP of 1.5 bar. The cross-flow velocity of the feed solution through the fibers was set at 4.5 m s^{-1} in order to reduce the effect of concentration polarization. This corresponds to a Reynolds number of approximately 3500, and is in the turbulent regime. We run the filtration set-up at extremely low recovery. That means that the concentration effect would be very small. In the case of wastewater filtration for MPs retention, membrane compaction was carried out at 1.5 bar for 2 h using demineralized water prior to feeding the filtration set-up with wastewater. Subsequently, permeate samples of the first 24 h of the filtration process were collected to measure the apparent rejection. Then a filtration duration of 48 h was applied in order to provide sufficient membrane saturation to ensure steady state rejections, and a sample was taken after this time. Kimura et al., [56] observed quasi-saturation of the membranes after about a 20-h filtration of hydrophobic compounds at low concentration (~ 100 ppb). To avoid overestimation of compounds rejection, they proposed longer filtration times in order to reach adequate membrane saturation whenever low concentrations of solutes exists in the water.

Concentration values of all salts were measured with a Cond 3210 conductivity meter purchased from Wissenschaftlich-Technische Werkstätten GmbH. Each measurement was performed in triplet and the average of values with standard deviation is reported just for twelfth and thirteenth layers of polymer. Retention (Re) in % was calculated using Eq. (4).

$$Re = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{4}$$

Where, C_P and C_F are solutes concentrations of permeate and feed solution, respectively.

For MPs analysis, samples of feed and permeate streams (duplicate samples) of the NF installation were shipped to the LaDrôme laboratory (in France) in a freeze box for analysis within 24 h under the analyzing license of COFRAC-ESSAIS. A multi detection procedure including Gas Chromatography (coupled with ECD/NPD mass spectrometry) and Liquid Chromatography (along with DAD, fluorescence, tandem mass spectrometry) was applied for all MPs with Limit of Quantification (LQ) of 0.01 μg/L for Diclofenac, Naproxen and Ibuprofen, and 0.04 μg/L for 4n-Nonylphenol. Then, as mentioned in Eq. (4), apparent (R_{app}) and steady-state rejection (R_{ste}) of MPs were determined.

3. Results and discussion

3.1. The hydraulic resistance of PEM based membranes

The hydraulic resistance of the PEM based membranes, prepared at an ionic strength of 50 mM $NaNO_3$, were measured for each deposited layer to observe the transition from the pore dominated regime to the layer dominated regime [49]. As it can be seen in Fig. 3, the hydraulic resistance generally increases after an additional coating step, in line with the increasing PEM layer thickness. Initially, the smaller increment in hydraulic resistance from bare fiber until the fourth deposited layer (part a) indicates that firstly pores become narrower. Then, the much sharper increase is observed between layers 4–9 (part b), indicating the pores becoming fully filled with the PEM layer. After that, the resistance increases much slower again (part c), an increase simply related to the increasing thickness of the PEM coating. The sharp transition between layer 4 and 9 is a first clear indication of a transition from a pore dominated to a layer dominated regime. More evidence comes from the observed zig-zag behavior, which is related to the so-called odd-even effect. The final layer in a PEM can determine the degree of swelling of the whole layer, with PAH terminated layers being more swollen than PAA terminated layers. The change in swelling with different terminating layers leads to the zig-zag behavior. Initially, the resistance upon PAH adsorption (layer 3) shows a strong increase, which goes down when PAA is absorbed (layer 4). But for thicker layers (layer 12) PAA adsorption leads to an increase in resistance, while we see lower resistance for the 13th layer. This behavior (the flipping of the odd–even effect) also reflects a shift from the pore dominated regime to the layer dominated regime. In the pore dominated regime, the pores of the membrane are coated with the PEM, and an increase in swelling of that multilayer will result in a pore size decline and subsequently a reduced membrane permeability. While in the layer dominated regime, a dense layer is formed on top of the membrane and swelling of the layer leads to a more permeable layer and consequently a lower resistance [49]. From the observed behavior, we can be certain

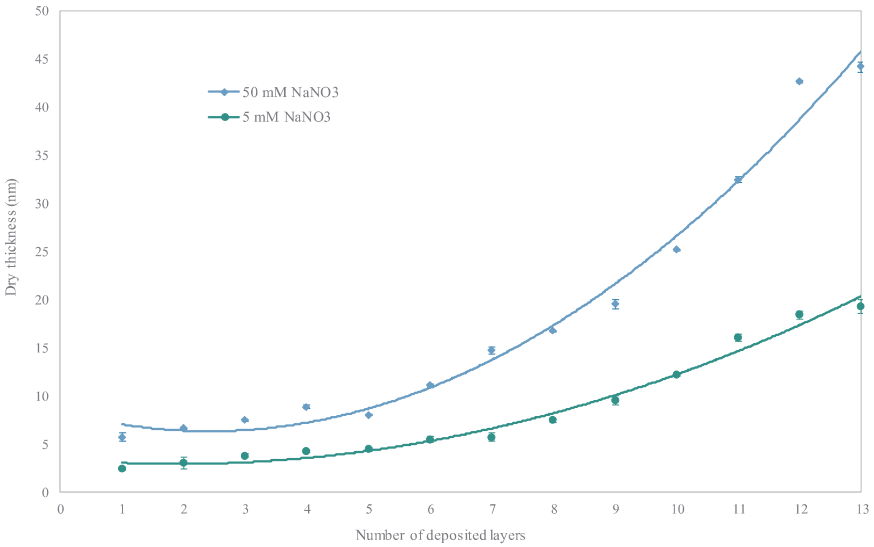

Fig. 4. Comparison of ellipsometric dry thicknesses of each deposited layer in two ionic strengths of 5 and 50 mM $NaNO_3$.

that we are well within the layer dominated regime, and that any separation will be dominated by the PEM coating, rather than the original membrane pores.

3.2. The influence of ionic strength on the PEMs performance

To compare the properties of coated membranes at different ionic strengths, PEMs were also prepared at the lower ionic strength of 5 mM of $NaNO_3$. Lowering the ionic strength used for PEM preparation is known to lead to denser PEM layers, with better separation properties and lower permeabilities [50], but it has not been investigated for this type of polyelectrolyte system (PAH/PAA). Fig. 2S in Supplementary Data compares pure water permeabilities of the PEMs-based membranes made in this study with the common commercial UF, NF and RO membranes. In this figure, we show that permeability of our membranes is lower than UF and most of NF membranes, while it is mostly close to RO membranes. To compare the PEM growth under different conditions, ellipsometric thicknesses of PEMs on model surfaces along with hydraulic resistances of the prepared membranes were obtained.

Fig. 4 compares the dry thicknesses of adsorbed multilayers in two ionic strengths. After 13 layers, the PEM prepared at the lower ionic strength is about 2.3 times thinner than its counterpart. When polyelectrolyte assembly takes place at a low ionic strength, the polymer chains are more extended, resulting in a thinner film. Increasing the ionic strength results in the coiling of the chains, which become less extended but increase the volume of a multilayer [78]. The hydration of a PEM is a very important parameter to predict membrane performance, as it shows how open the layer structure is. The hydration ratio of PEMs consisting of 12 and 13 layers was determined from the measured wet and dry ellipsometric thicknesses as shown in Fig. 5. From this data, it is evident that PEMs prepared under lower ionic strength have a lower hydration, and therefore the layers will be expected to act as a denser membrane. This is also observed from the measured hydraulic resistance (Fig. 6). While the layers prepared under higher ionic strength are about 2.3 times thicker, the resistance is only 1.5 or 1.25 times higher. As the resistance linearly scales with the thickness of a layer, this must mean that the PEMs prepared at 5 mM are denser and are expected to have a better separation performance.

3.3. Contact angle of PEMs

In Fig. 3S in Supplementary Data, we clearly show variations in the water contact angle among both positively and negatively-charged PEMs with two ionic strengths of 5 and 50 mM $NaNO_3$. A decrease in

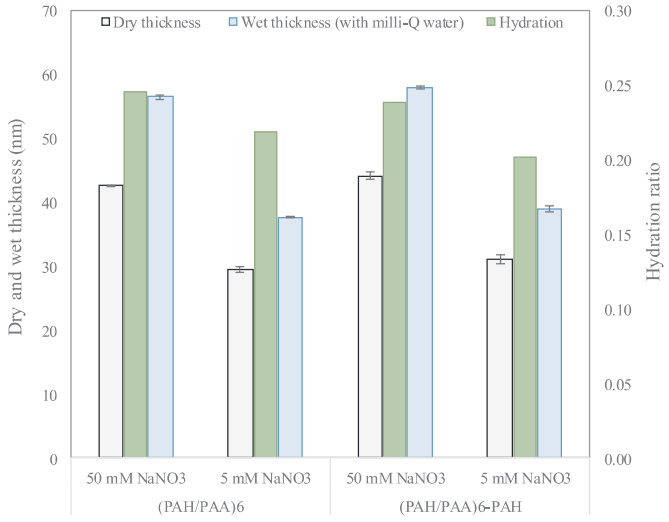

Fig. 5. Hydration, dry and wet thicknesses of membranes coated with $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers in two ionic strengths of 5 and 50 mM $NaNO_3$.

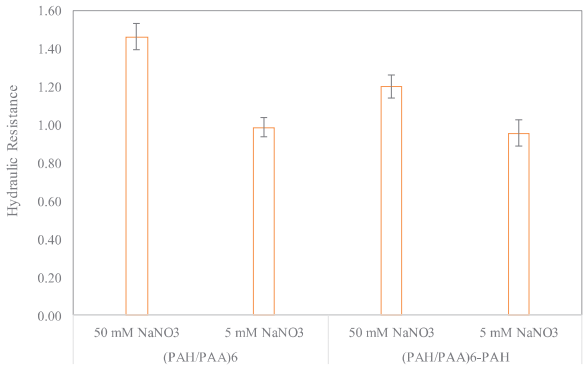

Fig. 6. Hydraulic resistance of membranes ($\times 10^{14}$ m^{-1}) coated with $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers in two ionic strengths of 5 and 50 mM $NaNO_3$.

contact angle was obtained after deposition of PEs (For instance 42.2 ± 1.6° and 42.4 ± 1.5° for silicon wafers and fibers, respectively coated with $(PAH/PAA)_6$ multilayers in 5 mM of $NaNO_3$) compared to bare HFS fiber that had a contact angle of 67.3 ± 0.3°. This phenomenon indicates that multilayers adsorption imparts hydrophilicity to the membrane surface. This finding is in accordance with study performed

by Fadhillah et al., [35] who verified PSF membrane with PAH/PAA multilayers where the decrease in contact angle was resulted after 60 bilayers (35.48 ± 6.38°) compared to bare PSF substrate with a contact angle of 79.8°. Membranes with hydrophilic surfaces are less susceptible to fouling and their fouling is often reversible [79]. This is due to membrane hydration by water molecules which act as a barrier for potential foulants. Furthermore, these water soluble PEs form loops and tails which increase surface charge density. This rise in surface charge density contributes in the hydrophilicity of the membrane [80]. There was a small amount of increase in the hydrophilicity of coated silicon wafers after a 48-h immersion in synthetic wastewater containing target MPs. This reduction in contact angle did not change after re-immersing them in milli-Q water for another 48 h, indicating that this change is irreversible. In a similar trend, contact angles of coated fibers declined a little after filtration of feed solution e.g. contact angles of clean and fouled fibers were 42.4 ± 1.5° and 36.3 ± 0.9°, respectively for $(PAH/PAA)_6$ multilayers coated with ionic strength of 5 mM $NaNO_3$. To the best of our knowledge, no literature data are available on contact angle changes after MPs rejection by NF membranes fabricated with PEMs, making comparison with the results of this study difficult.

3.4. Salts retention

PEM-based membranes, fabricated by the LbL assembly of PEs on hollow fiber support membranes, have been employed for ion rejection applications such as water softening or desalination [8]. In the category of NF membranes prepared with this method, membranes with high rejections of divalent ions and typically still significant rejections of monovalent ions have been studied [18]. Typically such membranes have two separation mechanisms (i) sieving in the case of species bigger than the membrane pore size and (ii) electric repulsion due to Donnan and dielectric effects in the case of charged species [81]. In the present work, the ion rejections were measured for three different ion pairs, namely NaCl, $CaCl_2$ and Na_2SO_4 at a concentration of 5 mM for all compounds. The results are presented in Fig. 7. For the both negatively and positively-charged membranes, the highest retention is obtained for the ion pair with the large SO_4^{2-} ion and a lower rejection is found for Ca^{2+} and Cl^- (the size order of the used ions is: $SO_4^{2-} > Ca^{2+} > Cl^- > Na^+$ [82]). On the other side, a higher SO_4^{2-} rejection is seen in negatively-charged membranes compared to the PAH-terminated membranes. This trend is also observed in the case of Ca^{2+} rejection, but with a lower difference between PAA and PAH-terminated membranes. This behavior, next to the fact that a little difference is observed between the membranes prepared at two ionic strengths, indicates that size exclusion followed by charge repulsion are

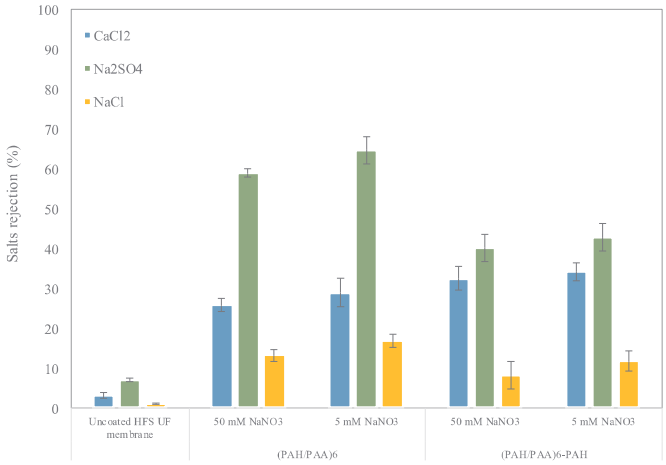

Fig. 7. Single salt rejection of HFS membranes coated with $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers in two ionic strengths under cross-flow filtration, at turbulent regime (Reynold number > 3500) and TMP of 1.5 bar.

the main mechanisms involved in salts retention by these membranes.

Fig. 7 also indicates that fibers coated with lower ionic strength have a somewhat higher salt rejection than membranes coated at higher ionic strength. For instance, Na_2SO_4 rejections of $(PAH/PAA)_6$ multilayers for ionic strengths of 5 and 50 mM $NaNO_3$ are 64.7 ± 3.5% and 59.0 ± 0.9%, respectively. This behavior comes from this fact that PEMs prepared under lower ionic strength have a more compact structure (lower hydration ratio illustrated in Fig. 5) with less open multilayers leading to better retention. The most important result shown in this figure, however, is that we have prepared a NF membrane with a very low ionic rejection, similar to the results of Ilyas et al. [27]. As mentioned, a low ion rejection would be highly beneficial; as such membranes would not create a brine waste stream. Still the low ion rejection is only relevant, if the MPs rejection of these membranes under conditions relevant to wastewater treatment, is high enough.

3.5. MPs rejection

The apparent and steady-state retention of MPs from synthetic secondary-treated wastewater was examined under filtration circumstances similar to those for the salts rejection tests. Then, relationships between physicochemical properties of MPs and their rejections were evaluated.

3.5.1. Apparent MPs rejection

In Fig. 8a, we report on the apparent rejection of our four target MPs for PAA and PAH terminated PEM membranes, prepared at 5 and 50 mM $NaNO_3$. The apparent rejection of the hydrophobic 4n-Nonylphenol is the highest for all cases, followed by Diclofenac and then Ibuprofen and Naproxen. Of the membranes, the PAA terminated membranes perform better than the PAH terminated membranes. This effect was also observed by Ilyas et al. [27] and was attributed to PAA terminated layers being more dense in nature. Another way to densify the membrane is by lowering the ionic strength of preparation, as also discussed in Section 3.2. In apparent rejection, adsorption of MPs to the membrane can significantly affect the results. That means that affinity between the membrane and the MPs can be a crucial parameter. We investigated the connection between the rejection and some of the molecular properties of the MPs (Fig. 9 and Fig. 4S in Supplementary Data). In this matter, a linear increase ($R^2 \geq 0.9$) between hydrophobicity (log D) and apparent rejection of all MPs was observed (Fig. 9). Additionally, no strong relation was found between the apparent rejection of MPs and their correspondent molecular weight and molecular sizes (molecular volume and molar volume) (Fig. 4S in Supplementary Data). This gives a strong indication that affinity dominates the apparent rejection, with more hydrophobic MPs adsorbing more to the membrane surface. This can be due to the PEM layer, but more likely the adsorption takes place to the more hydrophobic PES support membrane.

3.5.2. Steady-state MPs rejection

In comparison with apparent rejection, the steady state rejections are lower for all investigated membranes (Fig. 8b). After reaching to steady-state condition, the membrane does not take up any MPs by adsorption, and other rejection mechanisms become dominant. This reduction is the most severe for the hydrophobic 4n-Nonylphenol (e.g. from 90.7 ± 0.1% to 70.1 ± 2.3% for 5 mM of $NaNO_3$ and $(PAH/PAA)_6$ multilayers), and is less notable for hydrophilic compounds. Consequently, in line with the findings of Yangali-Quintanilla et al. [59], we are not able to consider hydrophobic adsorption of MPs into the membrane surface as a long term rejection mechanism because diffusion through the membrane occurs over the time causing retention decadence after saturation of the membrane [59].

When comparing our prepared membranes, we again find that the membrane prepared at 5 mM and terminated with PAA outperforms the other membranes, although the effect is relatively small. The separation

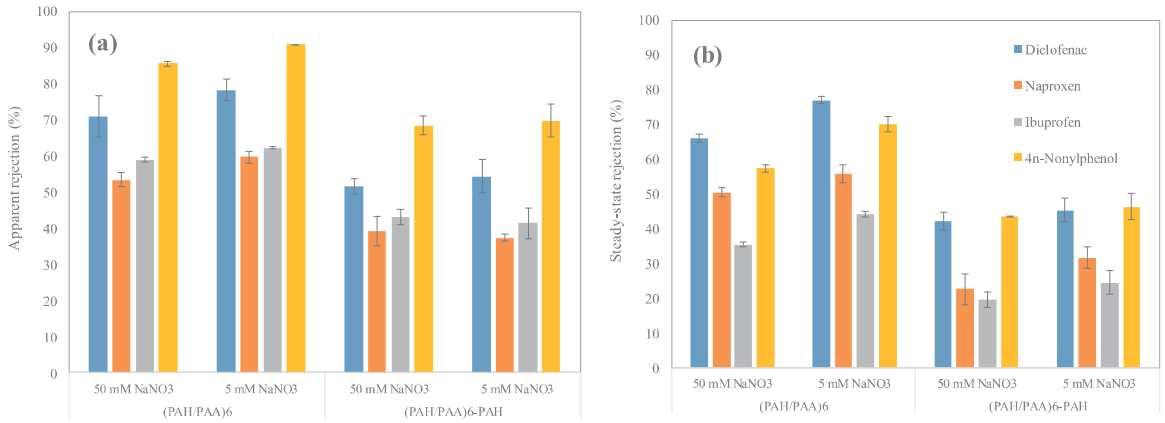

Fig. 8. Apparent (a) and steady-state rejection (b) of MPs in membranes coated with $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers (pH: 6/6 for both PEs) in two ionic strengths of 5 and 50 mM $NaNO_3$.

layer of this membrane is less hydrated compared to the others. In Fig. 8b we also show the rejection performance of the both $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers prepared under two ionic strengths is in accordance with those observed for the salt rejection. On one hand, the rejection performance of the membranes prepared at 5 mM $NaNO_3$ is still somewhat higher for all MPs as a result of lower hydration compared with its counterpart described in Section 3.2. For instance, rejection of Diclofenac for $(PAH/PAA)_6$ multilayers was 76.9 ± 1.1% versus 65.8 ± 1.2% for 5 and 50 mM $NaNO_3$, respectively. On the other side, in the case of the PAA-terminated PEMs, rejection mechanism of charge repulsion observed for negatively-charged MPs as though these negative-surface membranes showed about 32%, 24% and 20% of higher retention for Diclofenac, Naproxen and Ibuprofen, respectively than PAH-terminated PEMs for ionic strength of 5 mM $NaNO_3$. This evidence is what we saw in the case of SO_4^{-2} rejection by negatively-charged membrane. The higher rejection even also occurred for neutral 4n-Nonylphenol probably as a result of more-dense surface of PAA-terminated PEMs compared with PAH-terminated ones. As there is no charge involved in the rejection of 4n-Nonylphenol, we believe that its steady-state rejection is fundamentally based on size exclusion and still hydrophobic adsorption. Jermann et al., [83] indicated that Ibuprofen (up to 25%) and Estradiol (up to 80%) can be removed in hydrophobic UF membranes via adsorption onto membrane polymers, as well as interaction with natural organic matter in wastewater. Furthermore, it seems that long-shaped molecular geometry of 4n-Nonylphenol should be also taken into account in the retention adequacy since it can easily pass through the membrane's pores.

Relationship between steady-state rejection of MPs and their relevant molecular weights (Fig. 10) represent that compounds of larger molecular weights are relatively better rejected even though the R-squared values of these linear curves are not gratifying. Meanwhile, as shown in Fig. 5S in Supplementary Data, parameters of log D, molecular and molar volume did not show striking correlation with steady-state rejection of all MPs. These results are in full agreement with the outcomes of Van der Bruggen et al. [84] who concluded that molecular weight can be a convenient representative of NF performance for retention of a series of organic molecules (molecular weight of 32–697 g mol^{-1} and stokes diameter of 0.51–2.65 nm) compared with other molecular sizes.

In addition, as plotted in Fig. 11, we could also find a good correlation ($R^2 \geq$ 0.70–0.97) between the steady-state rejection of charged MPs with their relevant MPA. Although the MPA was found as a better surrogate parameter in comparison to molecular weight, we do believe that much more research needs to be done to understand the MPs rejection by LbL-made NF membranes. In the case of commercial membranes, Fujioka et al. [85] reported that the rejection of charged MPs is high (over 90%) by hollow fiber cellulose triacetate RO membranes when the MPA of the compounds is over 35 $Å^2$ like this study. Conversely, there was not a strong correlation between the rejection of charged MPs and their MPA by the ceramic NF membranes in the observations of Fujioka et al. [44]. Kiso et al. [86], who investigated the effect of molecular shape on rejection of uncharged organic compounds, concluded that molecular width is a major factor controlling solute permeation in NF membranes. Similarly, Madsen and Søgaard [87] obtained the best relationships between the pesticides rejection by NF membranes and their molecular width. Hence, it seems that spatial

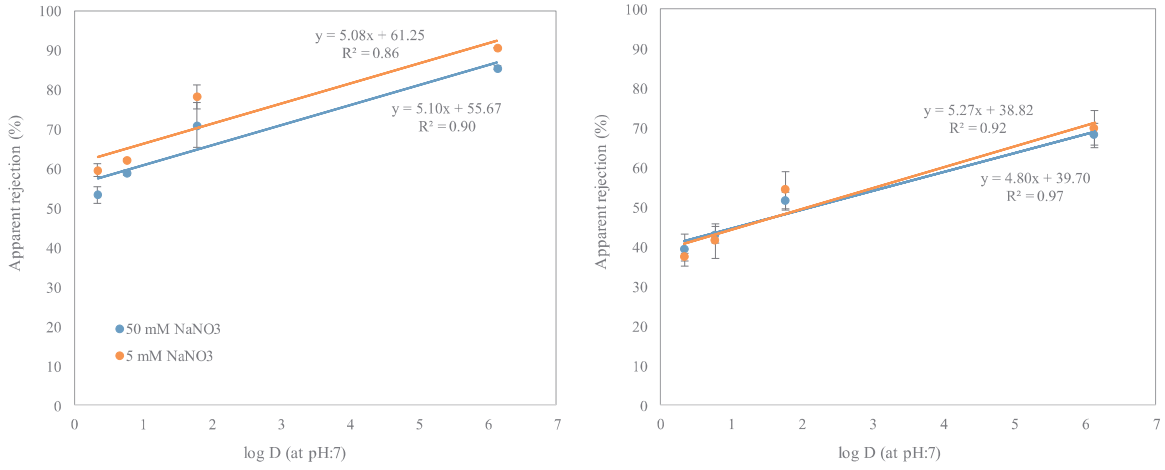

Fig. 9. The correlation between apparent rejection and hydrophobicity of MPs (Left and right figures are related to $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers, respectively).

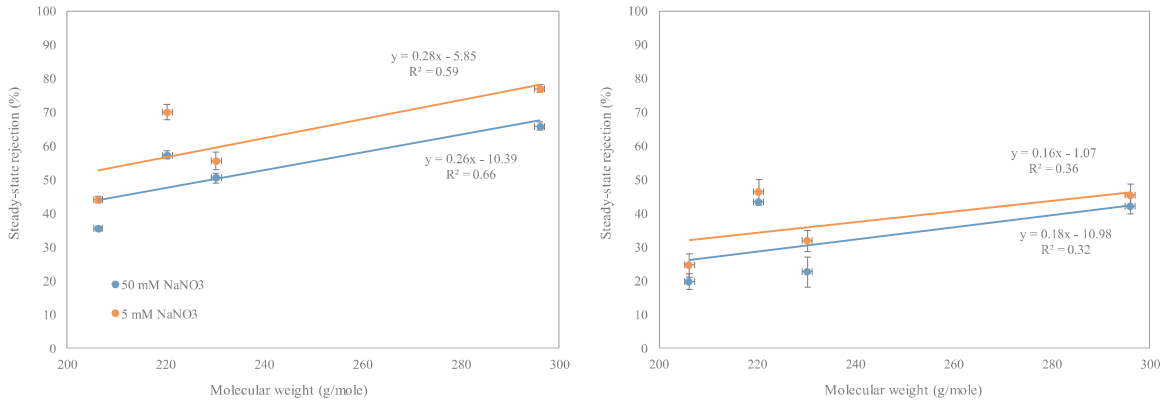

Fig. 10. The correlation between steady-state rejection and molecular weight of MPs (Left and right figures are related to $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers, respectively).

dimensions that determine the movement and rotation of the molecules outperform the molecular weights in the rejection behavior of the membranes. Having a look at the 4n-Nonylphenol's molecular shape (Table 2) shows the long-shaped geometry of this molecule should be taken into account in the retention adequacy since it could easily pass through the membrane's pores.

3.5.3. Comparison of LbL-made NF membranes with commercial NF membranes in salts and MPs removal

When we now combine the data from Figs. 7 and 8b, we find that we have indeed prepared a membrane (PAA-terminated PEMs, prepared at 5 mM $NaNO_3$) with a very reasonable removal of MPs (around 45–80%) under relevant conditions for wastewater treatment, with and a very low ionic rejections (nearly 17% NaCl). It becomes clear how unique this membrane is when we compare our results to commercial NF membranes that have been applied to MPs removal. In Fig. 12, we compare the rejection of target MPs and NaCl simultaneously from commercial NF membranes found in literature and our best LbL-made NF membranes. More details about the type of feed, membrane and operational conditions are given in Table 1S in Supplementary Data. This data shows clearly that commercial NF membranes reject both MPs and salts to a great extent while the membranes prepared in this study rejected salts only slightly and MPs considerably. For example, commercial NF membranes could retain NaCl and Diclofenac up to 70–90% and 99–100%, respectively while these rejections have occurred by 16.8 ± 1.6% and 76.9 ± 1.1%, respectively for our PEMs. Thus, a big advantage of our LbL-made NF membrane is that it could be used for MPs removal without producing a salty concentrate. Compared to the commercial membranes, that have been optimized towards high Donnan and Di-electric exclusion, we believe that size exclusion is the dominant mechanism for MP removal with our LbL based membranes.

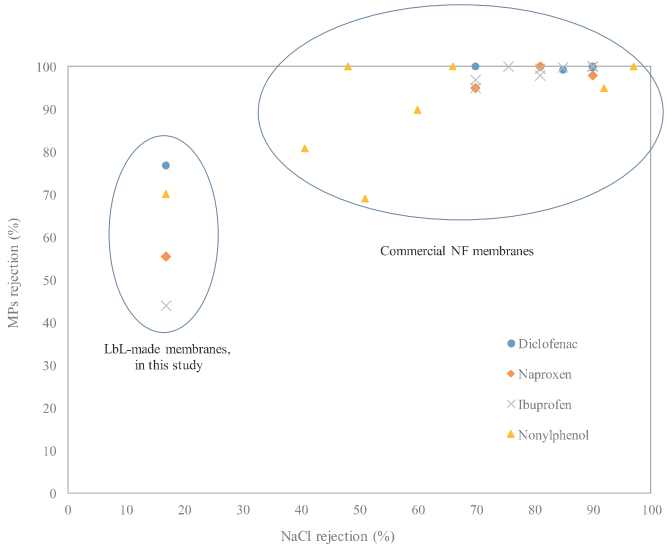

Fig. 12. Simultaneous rejection of target MPs and NaCl using commercial NF membranes found in literature (Table 1S in Supplementary Data), and LbL-based NF membranes made with $(PAH/PAA)_6$ multilayers prepared in ionic strength of 5 mM $NaNO_3$.

Still, the exact separation mechanism will need to be studied in much more detail in the future. We strongly expect that with further optimization, for example by coating at even lower ionic strengths, that even higher MPs removals can be attained at still low NaCl rejections. This makes this type of membrane very interesting for use as a tertiary treatment step for wastewater treatment plants, of which the concentrate can be treated in a bioreactor as discussed in the introduction.

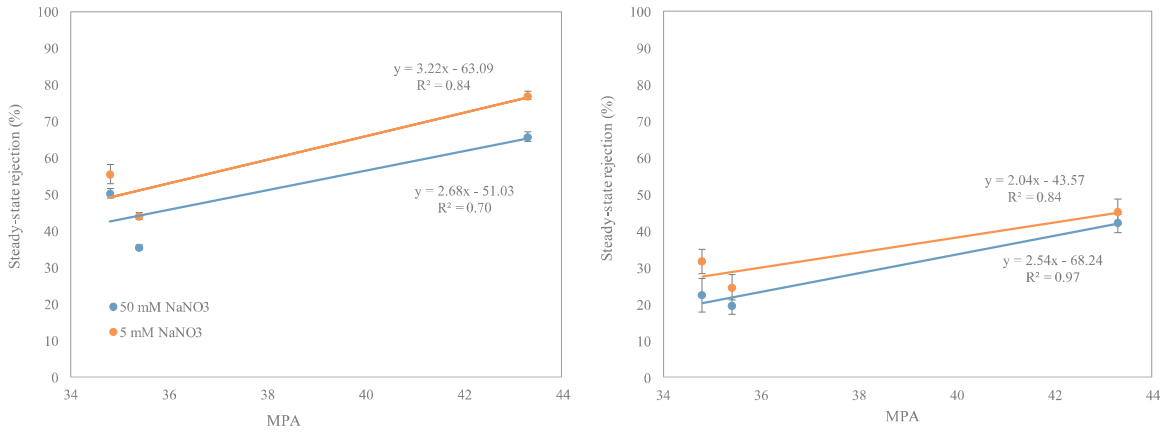

Fig. 11. The correlation between steady-state rejection and MPA ($Å^2$)of charged MPs (Left and right figures are related to $(PAH/PAA)_6$ and $(PAH/PAA)_6$-PAH multilayers, respectively).

Moreover, as the salt balance of the effluent will not be changed dramatically after passing through these PEMs-based membranes, the effluent could be used for the irrigation of agricultural crops that are sensitive to salinity balance of the water used [88,89].

4. Conclusion

The scientific community is currently faced with the important challenge of MPs accumulation in aquatic environments. For this reason, various tertiary treatment methods are proposed to efficiently remove MPs from the wastewater effluent. In the present work, we provide further insights into the key parameters involved in apparent and steady-state rejections of MPs by NF membranes made with LbL adsorption of weak PEs on the surface of hollow fiber UF membrane. In addition, the effect of ionic strengths on the properties of PEMs was studied as this parameter determines the charge compensation of the PEs in the multilayer [49] and thereby the hydration and the effective pore size of the membrane. Here, we prove that PEMs prepared in lower ionic strength and terminated with PAA are more efficient in salts and MPs removal as they were found to be thinner and less open. We also demonstrate that it is possible to achieve good MPs rejections at realistic wastewater treatment conditions, combined with low ionic rejections. Lower rejection of salts will be much more favorable for biological treatment of the retentate stream. In addition, these membranes do not significantly disturb the salinity balance of the effluent, making the filtered effluent much more appropriate for use, for example, irrigation water. Considering these capabilities, low ion retentions and high MPs retentions would possibly enable these membranes to outperform currently available commercial NF membranes for MPs removal from municipals wastewater effluents.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2017.10.045.

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